

学校编码: 10384

学号: 20620101151423

分类号__密级__

UDC__

厦 门 大 学

硕 士 学 位 论 文

液相溶胶包裹修饰法制备煤制天然气甲烷 化催化剂的研究

Study on the Coal to Substitute Natural Gas Methanation

Catalysts Prepared by Liquid Sol Coated Modification

Method

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论文提交日期: 2013 年 6 月

论文答辩时间: 2013 年 月

学位授予日期: 2013 年 月

答辩委员会主席: _____

评 阅 人: _____

2013 年 6 月

The Master Dissertation of Science in Xiamen University

**Study on the Coal to Substitute Natural Gas Methanation
Catalysts Prepared by Liquid Sol Coated Modification
Method**

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摘 要

鉴于当今的能源现状、全世界对环境保护的诉求以及我国的能源储量结构，合理高效地使用煤炭资源越来越凸显重要性。煤炭利用技术已经在以合成氨为主要代表的行业大量应用，相关技术日渐成熟，尤其是煤制代用天然气。但是，煤制天然气过程的关键技术之一是合成气制甲烷，其中尚存在若干问题需要解决。例如，镍基催化剂作为主流的甲烷化催化剂其抗硫性差、高温下易烧结和积碳失活、活性组分与载体作用太强等缺点还有待弥补。

为了寻求性能更佳的甲烷化催化剂，本论文基于固定床管式反应器对制备的一系列催化剂进行活性评价，并运用一系列表征手段对催化剂进行测试，最终确定了最佳的复合载体 $\text{MgO-Al}_2\text{O}_3$ 以及最佳复合载体中 MgO 的含量。此外，考察了焙烧温度、金属助剂 La 和活性组分 Co 的添加对催化剂活性的影响。

本文研究获得的主要结果如下。

(1) 采用液相溶胶包裹修饰法制备了系列 $\text{NiO/MO}_x\text{-Al}_2\text{O}_3$ ($\text{M}=\text{Si}, \text{Zr}, \text{Mg}$) 催化剂。反应前在 $10\%\text{H}_2/\text{N}_2$ 气氛下 400°C 还原 3h。考察不同复合载体对催化剂活性的影响。结果表明，加入 Si 、 Zr 和 Mg 后，活性组分 Ni 与载体 Al_2O_3 之间的相互作用得以减弱，利于催化剂在低温下的还原。系列 $\text{NiO/MO}_x\text{-Al}_2\text{O}_3$ 催化剂的活性明显依赖于载体中添加的第二金属氧化物的种类。不同载体所制镍基催化剂中 CO 转化率依次为： $\text{NiO/MgO-Al}_2\text{O}_3 > \text{NiO/ZrO}_2\text{-Al}_2\text{O}_3 > \text{NiO/SiO}_2\text{-Al}_2\text{O}_3 > \text{NiO/Al}_2\text{O}_3$ 。

(2) 在催化剂 $\text{NiO/MgO-Al}_2\text{O}_3$ 中，使 MgO 含量在 0%-20%（以催化剂为基准的重量百分比，下同）之间变化，以考察 MgO 添加量对催化活性的影响。研究结果表明，当 MgO 含量为 10% 时，对催化剂活性的促进作用最大，在各反应温度下均表现出比其他 MgO 含量的催化剂更高的活性。同时发现，高 MgO 添加量（20%）的催化剂较之低 MgO 添加量（5%）的催化剂更适合在高温下反应。利用 X 射线衍射(XRD)、氮气吸附脱附(BET)、程序升温还原(TPR)、二氧化碳程序升温脱附($\text{CO}_2\text{-TPD}$)等表征方法对催化剂进行研究，结果可见，由于 MgO 的晶格大小与 NiO 相近，可以在晶胞中与 NiO 互换，与 NiO 形成固溶体，其结果是 MgO 替代了一部分 NiO 与载体 Al_2O_3 紧密结合，使得催化剂表面的游离镍

增多，从而促进氢在催化剂表面的吸附。而表面吸附的氢越多，在催化剂表面由 CO 分解生成的活性碳物种以及氧物种能够加速转化为 CH_4 和 CO_2 ，促进催化剂吸附的 CO 从催化剂表面脱除释放，从而为 CO 的再吸附提供新的活性位点，加速了 CO 的吸附。在这个过程中，CO 转化反应速率提升，即催化剂的活性得到提高。

(3)将上述所制高活性 10%NiO/10%MgO- Al_2O_3 催化剂分别在 400°C、500°C 和 600°C 温度下焙烧，结果表明焙烧温度对催化剂活性有显著影响。提高焙烧温度使得活性组分 Ni 与载体 Al_2O_3 之间的相互作用增强，导致活性组分镍更难于在低温下还原，最终造成催化剂甲烷化活性大幅度降低。

(4)通过单因素考量 La_2O_3 含量不同对催化剂活性有影响后，结合 MgO 添加量和焙烧温度，采用正交试验方法，综合考察了以上三个因素对催化剂活性的影响。结果显示，在本文所选择的因素水平条件下，以焙烧温度对催化剂活性的影响为最大。在所设定的条件下，5% La_2O_3 -5%MgO-400°C 的催化剂甲烷化性能最佳。助剂 La_2O_3 在催化剂中主要是通过促进 NiO 在载体 Al_2O_3 表面的分散，以及减弱 NiO 与载体之间的相互作用而起作用。

(5)添加 Co 作为甲烷化催化剂的第二活性组分 Co，结合还原温度与焙烧温度，综合分析了各因素对催化剂活性影响的大小。经过方差分析得到：对于给定的显著性水平 α ，焙烧温度和钴镍比对催化剂活性有高度显著的影响，还原温度对催化剂活性有显著的影响，还原温度和焙烧温度的交互作用对催化剂活性有影响。固定 Ni 含量的条件下，在本文试验条件范围内，Co 添加量越大，催化剂活性越高。

关键词：

镍基催化剂；CO 甲烷化；液相溶胶包裹修饰法；复合载体；表面碳；活性组分；游离镍

Abstract

In the light of the situation of the energy supply, universal environmental protection appeal and the energy resource structure of our country, how to use the coal resources efficiently has been more and more important. The technologies for coal utilization technology have been applied greatly in many fields, represented by synthetic ammonia industry. Its relevant technology has matured, especially for coal synthesis gas. The crucial step to this technology is the technology from syngas to methane, which still leaves some questions need to be solved. For example, as current main catalyst, Ni-based catalysts' sulfur resistance are bad, and conventional nickel catalysts easily suffer from severe deactivation resulting from sintering of Ni particles and coke disposition during the exothermic methanation reaction. Also, the interaction between the active component and the support is too strong. All these defects are needed to be overcome.

In order to obtain more efficient catalysts for methanation, based on fixed bed reactor, the best composite support $\text{MgO-Al}_2\text{O}_3$ and the optimal contents of MgO has confirmed via testing and characterizing the series catalysts in this dissertation. The effects of calcined temperature, La content and Co content on the performance of supported catalysts are also studied.

The predominant results obtained are generalized as follows:

(1) By using liquid sol coated modification method, series of $\text{NiO/MO}_x\text{-Al}_2\text{O}_3$ ($\text{M}=\text{Si, Zr, Mg}$) catalysts were prepared. Before the reaction, all catalysts were reduced in $10\%\text{H}_2/\text{N}_2$ atmosphere for 3h to explore the effect of composite oxide supports on the catalytic performance of Ni-based catalysts. It was found that the interaction between the active component Ni and the support Al_2O_3 were weakened after incorporating Si, Zr, Mg, which was beneficial for catalyst reducing at low temperature. The catalytic performance of the $\text{NiO/MO}_x\text{-Al}_2\text{O}_3$ catalyst was found to be different, depending on the identity of second metal oxides (MO_x) added. The activity trend of different $\text{NiO/MO}_x\text{-Al}_2\text{O}_3$ catalysts followed: $\text{NiO/MgO-Al}_2\text{O}_3 > \text{NiO/ZrO}_2\text{-Al}_2\text{O}_3 > \text{NiO/SiO}_2\text{-Al}_2\text{O}_3 > \text{NiO/Al}_2\text{O}_3$.

(2) According to the investigation of the effect of MgO contents, from 0% to 20% (mass ratio), in NiO/MgO-Al₂O₃ on the catalytic performance, we discovered that methanation activity reached the highest, assuming the better activity than other catalysts with the different MgO loadings at every reaction temperature when MgO loadings got 10%. Also, 20% MgO loading catalyst trended to perform catalytic reaction at high temperature than 5% MgO loading catalyst. The catalysts were characterized by XRD, BET, TPR and CO₂-TPD. The results obtained indicate that: MgO crystal lattice is similar to NiO lattice in size, thus it can be interchangeable with NiO, forming solid solution with it, whose results are MgO substituting for a part of NiO to combination with Al₂O₃ tightly. All these makes the free nickel on catalyst surface increasing and promotes hydrogen adsorption on the catalyst surface. When the hydrogen in the ambience is enough, surface carbon and oxygen species formed through CO dissociation would speedily convert to CH₄ and CO₂ and desquamate from the surface to provide adsorption center for CO re-adsorbed and consequently accelerate CO adsorption. As a result, CO conversion rate speeds up and the catalyst performance improves.

(3) The high activity 10%NiO/10%MgO-Al₂O₃ catalyst prepared above were calcinated at 400°C, 500°C and 600°C, the result implied that different calcination temperature makes great difference to catalyst activity. The interaction between the active component Ni and the support Al₂O₃ is strengthened during calcination process, whose result is that the reduction of NiO becomes hard, bringing about the methanation activity decreasing greatly.

(4) After searching into the effect of La₂O₃ loadings on catalyst by single factor analysis method, integrating with MgO loadings and calcination temperature, we synthetically explored these three factors' effects on catalysts adopting orthogonal experiment. The results showed that calcination temperature makes the greatest influence on catalytic performance under the factor levels we selected. The

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